Didymium-Fe-B Sintered Permanent Magnets

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Present works describe the developments the low cost R-Fe-B sintered permanent magnets. Three different didymiums are chosen for the low cost mixtures of rare-earth elements. The studied alloy compositions are Fe-(32.5–34.5)wt. %R-(1–1.6)wt. %B, where R elements are didymium (Nd-10wt. %Pr), 5Ce-didymium (Nd-15%Pr-5%Ce), and 40 Ce-didymium (Nd-10%Pr-40%Ce). The specimens were prepared by the conventional powder metallurgical techniques. The best magnetic properties obtained in these studies are Br = 13.2 kG, *iHc* = 10.2 kOe, and $(BH)\max = 40$ MGOe with the Fe-33.5% (5Ce-didymium)-1%B alloy. Temperature dependence of *iHc* of this alloy is almost comparable to that of the Nd-Fe-B alloys.

INTRODUCTION

The increasing demands of the high performance samarium-cobalt permanent magnets urge to develop the new classes of materials, because of the short supply of relatively expensive samarium and cobalt. Newly developed R-Fe-B alloys[1–3] have the technological potential to replace some classes of samarium-cobalt magnets (R; rare earth elements).

Sagawa *et al.*[3] reported that the sintered Nd-Fe-B alloys had the magnetic properties up to $(BH)\max = 36$ MGOe. The high magnetic properties of Nd-Fe-B alloys are due to the intermetallic compound of $Nd_2Fe_{14}B$.[2,4,5] Croat *et al.*[4] identified the crystal structure of this compound as new tetragonal phase with $a = 8.80$ Å, $c = 12.19$ Å, by neutron diffraction. The same tetragonal $R_2Fe_{14}B$ phase is formed with the various rare earth elements such as Ce, Pr, Sm, Gd, Tb, Dy, Er, Ho, Tm, and Y.[2,3,5]

The purpose of the present investigation is to develop the low cost R-Fe-B permanent magnets in selecting the low cost R elements among available various rare-earth elements. Good candidate rare-earth elements for this purpose is the family of so called "didymium". Figure 1 shows an example of the extraction process of rare-earth elements from ores.[6] Extracting the La and some of Ce from the light rare-earth portion in Fig. 1, its remnants are called as didymium which is the mixture of Nd, Pr, and Ce. The didymium is then abundant and inexpensive.

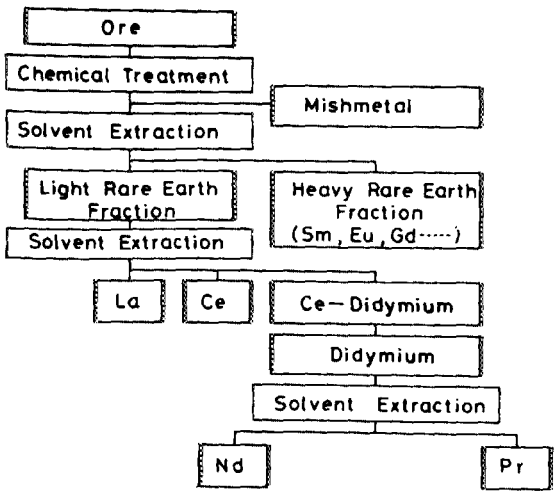

FIG. 1. Schematic illustration of extraction process of the rare earth elements from ores.

One might say that a mischmetal will be also abundant and inexpensive, and is the good candidate for low cost R-Fe-B magnets. But it is reported that La, which is the main constituent of the mischmetal, does not form the $R_2Fe_{14}B$ compounds.[2,5] Thus, didymium will be better candidate for developing the low cost R-Fe-B permanent magnets. Here we report the studies of the low cost didymium-Fe-B sintered magnets with energy products as high as 40 MGOe.

EXPERIMENTAL PROCEDURE

The selected compositions of the didymium were Nd-10 wt. %Pr (Didym), Nd-15%Pr-5%Ce(5CeDidym), and Nd-10%Pr-40%Ce(40CeDidym), which are the typical products in the extracting-process of the rare-earth elements. The studied compositions of R-Fe-B alloys are Fe-(32.5–34.5)wt. %R-(1–1.6)wt. %B, where R elements are Didym, 5CeDidym, and 40CeDidym. Chemical analysis shows that the total rare-earth content in these didymium is above 98.5 wt. %.

The alloys are induction melted from 99.9% electric iron, 98.5% didymium, and 99.9% crystal boron under an argon atmosphere. The ingots were crushed into 250 mesh powders and then ball milled to about 3–4 μm in alcohol. The powders were pressed into the compact of 1.5 cm in diameter, in a magnetic field of 10 kOe at a pressure of 1500 kg/cm^2. The green compacts were sintered at 1020–1100 °C for 4 h in an argon atmosphere and then were cooled at a rate of 50 °C/h to 150–200 °C.

Magnetic properties of the alloys are measured by applying the maximum magnetic field of 20 kOe. Temperature dependence of the coercivity (*iHc*) is measured on the sintered specimens parallel to its magnetically oriented direction with 15 kOe by vibrating sample magnetometer (VSM). The Curie temperatures of the sintered magnets should be estimated by the low field, but for the convenience, they measured in a magnetic field of 10 kOe by VSM. The microstructures of the sintered specimen were studied by electron probe microanalysis.

RESULTS AND DISCUSSION

Figure 2 shows the variation in the magnetic properties and the density of sintered Fe-(32.5–34.5)Didym-(1–1.6)B alloys versus sintering temperatures. The magnetic properties

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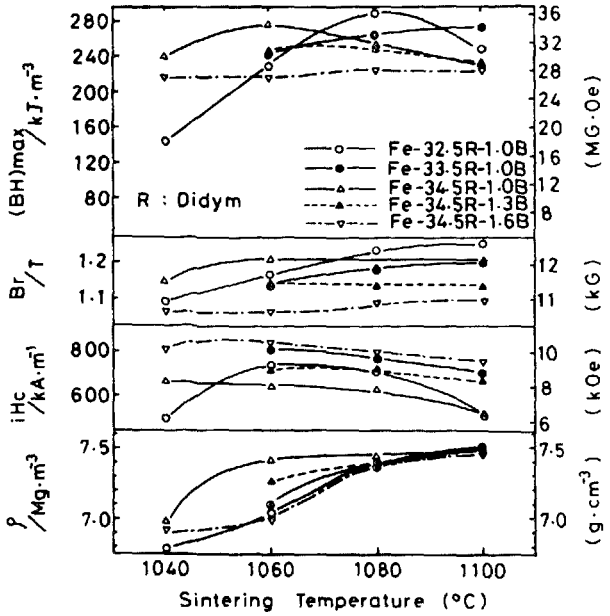

FIG. 2. Magnetic properties and density vs sintering temperatures of Fe-(32.5–34.5)Didymium-(1–1.6)B alloys.

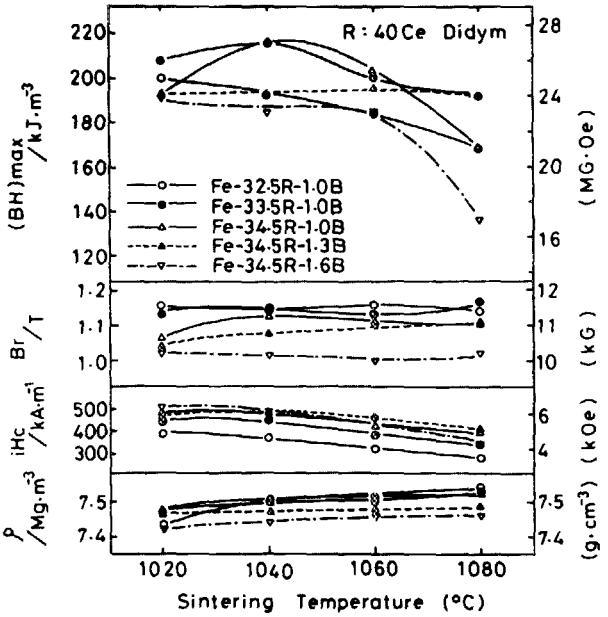

FIG. 4. Magnetic properties and density vs sintering temperatures of Fe-(32.5–34.5)40CeDidymium-(1–1.6)B alloys.

and the density shown here, are measured after the alloys are cooled to 150–200 °C at a rate of 50 °C/h. Density of the sintered products as high as 98%–99% of that of the cast alloys are achieved at sintering temperatures above 1080 °C. But the density of the alloy sintered below 1080 °C, decreases with decreasing the temperatures, indicating that the densification does not proceed well. Intrinsic coercive force *iHc* of Fe-34.5Didym-(1–1.6)B alloys increases with increasing the B content from 1% to 1.6%. Characteristics of the Fe-Didym-B alloys are such that the magnetic properties are varied very much with sintering temperatures and the content of didymium and B. The highest magnetic properties are attained with the Fe-32.5Didym-1B alloy as $Br = 12.4$ kG, iHc-10 kOe, and $(BH)\text{max} = 36$ MGOe.

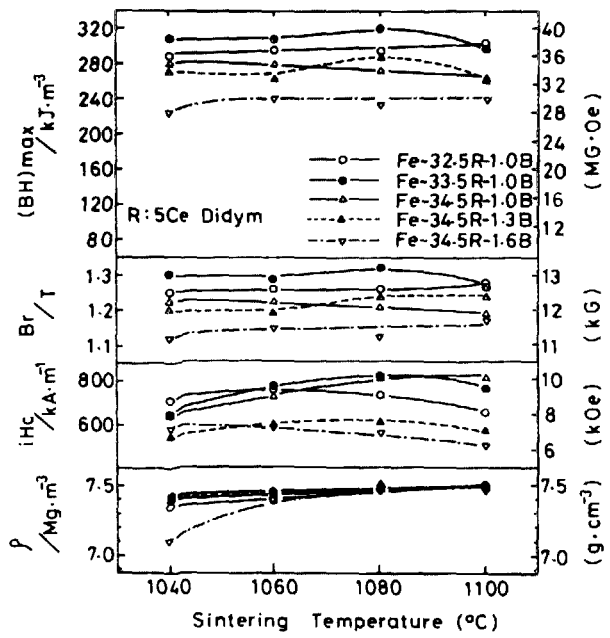

FIG. 3. Magnetic properties and density vs sintering temepratures of Fe-(32.5–34.5)5CeDidymium-(1-1.6)B alloys.

Figure 3 shows the magnetic properties and the density of Fe-5 CeDidym-B alloys versus sintering temperatures. Density of nearly 97%–99% of that of cast alloy is obtained for almost any studied 5CeDidym alloys after sintering at 1040–1100 °C. These good density products indicate that the densification proceeds well for 5CeDidym alloys, which reflects to the magnetic properties. The properties remain almost constant with varying the sintering temperatures (1040–1100 °C). Best magnetic properties are attained with Fe-33.5(5CeDidym)-1B alloy after sintering at 1080 °C as $Br = 13.2$ kG, $iHc = 10.2$ kOe and $(BH)\text{max} = 40$ MGOe.

Figure 4 shows the magnetic properties and the density of the Fe-40CeDidym-B alloys versus sintering temperatures. The density of sintered specimens reaches 97%–99% of the cast alloy for any compositional alloys. *iHc* of the Fe-(32.5–34.5) 40CeDidym-1B increases with increasing R contents. It should be noted that suitable sintering temperatures become around 1040 °C, which is lower than that of Didym and 5CeDidym alloys. An Fe-33.5(40CeDidym)-1B alloy sintered at 1040 °C gives the best magnetic properties as $Br = 11.5$ kG, $iHc = 5.3$ KOe, and $(BH)\text{max} = 27$ MGOe.

Figure 5 shows the scanning electron micrographs of the sintered Fe-33.5(5CeDidym)-1B alloy with $(BH)\text{max} = 40$ MGOe. Figures 5(b), 5(c), and 5(d) are the x-ray compositional images, using Fe$K\alpha$, Nd$L\alpha$, and Ce$L\alpha$, respectively. Figure 5(b) shows that Fe distributed within the $R_2Fe_{14}B$ grain, but the Nd-rich phase with white contrast existed along the grain boundaries as shown in Fig. 5(c). This observation is consistent with that reported before.[3] Figure 5(d) also indicates that Ce rich phase with white contrast existed along the grain boundaries, yielding the same behavior as the Nd-rich phase. But the Ce rich phase is much clearly imaged along the grain boundaries, for an example, denoting by arrow in Fig. 5(d). Thus it can be said that Ce

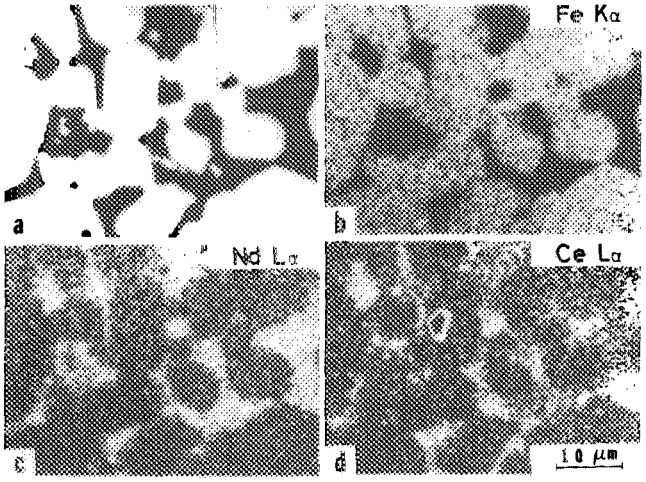

FIG. 5. Scanning electron micrographs of the Fe-33.5(5CeDidymium)-1B alloy, imaged with (a) absorbed electron, (b) Fe$K\alpha$, (c) Nd$L\alpha$, and (d) Ce$L\alpha$ x-ray.

rich phase could act as sintering aid as Nd-rich phase did. It is then speculated that good densifications of 5Ce or 40Ce-Didym alloys are due to the two effects of Ce. One is forming the Nd-Ce rich phase along grain boundaries. Melting points of Nd-Ce rich phase are lower than that of Nd rich phase (640 °C),[3] down to 600 °C according to the eutectic reaction in Ce-Fe binary phase diagram.[7] The other is lowering the melting point of $Nd_2Fe_{14}B$ compounds, by containing large amount of Ce. This could be the case of 40CeDidym alloys, which give the good properties after sintering at relatively low temperatures of 1040 °C. This is the good advantage for manufacturing CeDidym-Fe-B alloys.

The Curie temperatures of three typical sintered Fe-33.5R-1B alloys where R is (a) Didym, (b) 5CeDidym, and (c) 40CeDidym, measured at 10 KOe, are (a) 337 °C, (b) 332 °C, and (c) 298 °C, respectively. For references, the Curie temperature of the Fe-33.5Nd-1B alloy is also measured to be 337 °C. This temperature is slightly higher than the reported value of 312 °C, measured in a low magnetizing field, for the $Nd_{15}B_8Fe_{77}$ sintered magnets,[3] because applying the field of 10 KOe to specimen excited some magnetization intensity along the direction of magnetic field, resulting in increasing the Curie temperature. It is found that temperature dependencies of iHc of 5CeDidym and Didym alloys are almost same as that of the Fe-33.5Nd-1B alloy. But iHc of 40CeDidym alloy decrease rapidly, by about 65% of iHc of the room temperature, at 100 °C.

From economical point of view, newly developed didymium-Fe-B sintered magnets family are very much attractive. Didymium and Ce-Didym are abundant and are easily produced, so that the Ce-Didym price will be much cheaper than pure Nd or Pr. Pr in Fe-Didym-B alloys will play the same role of Nd since it is reported that $Pr_2Fe_{14}B$ compound produces almost same properties as those of $Nd_2Fe_{14}B$ compound.[2,5] In contrast with $Pr_2Fe_{14}B$ or $Nd_2Fe_{14}B$ compounds, it was also reported that $Ce_2Fe_{14}B$ compound does not yield the good magnetic properties,[2] since crystal anisotropy field of $Ce_2Fe_{14}B$ compound is almost 1/3 of that of $Nd_2Fe_{14}B$ compound.[5] Thus it was not expected that Ce-Didym alloys produce relatively good magnetic properties as high as $(BH)\max = 27$–40 MGOe. Aparting from the contribution of the crystal anisotropy of $Ce_2Fe_{14}B$ compound, Ce plays an important role in densification of the alloy as sintering aid, and in lowering the melting point of $(NdPr)_2Fe_{14}B$ compounds and making it possible to sinter at relatively low temperatures of 1040 °C. Economically, 40Ce-Didym alloys are most inexpensive, and give the energy product of 27 MGOe, but have the high temperature coefficient. Alternatively, 5CeDidym-Fe-B sintered magnets with $(BH)\max = 40$ MGOe, are most promising among the present studied low cost alloys, since temperature dependence of the properties is also comparable to those of Nd-Fe-B permanent magnet system. 5CeDidym magnets have also significant advantage in their processing, where they undergo easy densification better than Nd-Fe-B alloys in our laboratory.

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